Doctoral Dissertation
Doctoral Program in Material Science and Technology (37th Cycle)

Study of glass-ceramics and brazing alloys for joining oxide and non-oxide ceramic matrix composites in corrosive and high-temperature environments

Carla Malinverni

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Supervisors
Prof. Milena Salvo, Supervisor
Prof. Valentina Casalegno, Co-Supervisor

Doctoral Examination Committee
Prof. Enrico Bernardo, Referee, University of Padova, Italy
Prof. Roberto D'Ambrosio, Referee, Consiglio Nazionale delle Ricerche, Pisa, Italy

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Declaration

I hereby declare that, the contents and organisation of this dissertation constitute my own original work and does not compromise in any way the rights of third parties, including those relating to the security of personal data.

Carla Malinverni
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Summary

The scientific activity of this doctoral thesis focused on the study of the joining of non-oxide-based and oxide-based ceramic matrix composites (CMCs) developed in the framework of the European project called CEM-WAVE. The CMCs in this project are planned to be manufactured with an innovative production process using microwave-assisted chemical vapour infiltration technology, which can make CMCs sustainable to be used in energy-intensive sectors such as steelmaking and significantly reduce the costs for the manufacture of radiant tubes employed in this sector.

Three sections of a W-shaped radiant tube are proposed: for the first section operating at a high temperature (around 1200 °C), non-oxide-based CMCs (SiC/SiC) were employed, while for the section operating at a lower temperature (around 900 °C) oxide-based CMCs (Al_2O_3/(Al_2O_3-ZrO_2)) were chosen. For the last section of the tube, a ceramic inlay made of monolithic alumina was used. In this PhD thesis, different joining strategies and materials were studied to join each section of the radiant tube. Advanced ceramics and CMCs supplied by companies and universities were morphologically characterized by means of scanning electron microscopy and X-ray computed tomography. The coefficients of thermal expansion (CTEs) of the CMCs, which is a crucial parameter to consider in a joining process, was measured with the dilatometric analysis. The joining materials were chosen based on their CTEs comparable to that of the CMCs, thermodynamic stability, and wettability with the substrates. The tailoring and the characterization

of the joining materials are very crucial since they affect the performance of the joints, and the best joining processes were found to avoid any thermal degradation that may occur during the heat treatments.

In this doctoral thesis, several glass-ceramic systems with different compositions and brazing alloys from Titanium Brazing, Inc. were used as joining materials for both non-oxide-based and oxide-based CMCs. Three systems were identified as suitable joining materials for non-oxide-based CMCs: two glass-ceramics (a yttria-alumina-silica system called YAS and a silica-alumina-soda-calcia-zirconia system named SBANC_2), and a brazing alloy called TiBraze1450 composed of Ni-Cr-Fe-Ti. Other three systems were identified for joining oxide-based CMCs: two glass-ceramics named T1 and T2M characterized by having $Y_2Ti_2O_7$ as their main crystalline phase, and a brazing alloy called TiBraze200Nb consisting of Ti-Zr-Cu-Ni-Nb. The joints, obtained with the most suitable joining processes for each system, were morphologically and mechanically characterized using single-lap offset (SLO) shear tests. Furthermore, the most promising joints obtained were tested under harsh conditions, such as direct flame exposure tests, to recreate environments similar to their final application.

Concerning non-oxide-based CMCs, flat-joints obtained with YAS glass-ceramic measured an apparent shear strength of 61±12 MPa, and the failure was caused by delamination of the SiC/SiC composite.

Concerning oxide-based CMCs, T1 glass-ceramic joints showed excellent thermal cycling resistance while some cracks were present across the T2M glass-ceramic joints after flame tests. Oxide-based CMCs and their joints were also tested using 4-point bending tests conducted at room temperature and at 900°C by ENEA (Faenza, Italy). For Al_2O_3/(Al_2O_3-ZrO_2) butt-joints with TiBraze200Nb, the apparent shear strength was 49±8 MPa, resulting in the delamination of the composite. Furthermore, the joining of oxide-based CMCs to monolithic Al_2O_3 was carried out using the most successful candidates from oxide-based CMC joints, which delaminated after SLO mechanical tests and survived after direct-flame exposure tests.

In this thesis, additional work on the coating of advanced ceramics such as ZrC using glass-ceramic systems to protect ZrC against high-temperature oxidation is reported, where the presence of the coating reduced the formation of a ZrO_2 layer. Moreover, an initial investigation on the sintering of ZrC powders using electrical resistance flash sintering conducted at the Università di Trento is also mentioned.